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Abstract

Colloidal Isopressing involves formulating a slurry with a weakly attractive particle network that can be pre-consolidated to a high relative density by pressure filtration and still retain fluid-like characteristics. The pre-consolidated slurry is injected into an elastomeric mold and isopressed. Isopressing rapidly convert the slurry into an elastic body that can be removed from the mold without shape distortion. Not only is this process rapid, but since the water saturated compact produced by this method does not shrink during drying, it can also be converted into a dense body without a long drying period.

It is demonstrated that micron-size surface features, such as 5 μm wide channels with a depth/width ratio of 2, can be rapidly produced on the surface of alumina powder compacts. It was shown that surface features of this size were enabled when the saturated, isopressed body was strengthened. Namely, the fracturing of thin vertical portions of a micro patterned surface during pressure release and demolding is an obstacle to obtaining micron size features with high aspect ratios. It was shown that concentration controlled gelation of a PVA-Tyzor[®] TE additive effectively increased the strength of the elastic, isopressed body, saturated with water, while maintaining the low viscosity of the pre-consolidated body, which is required for transferring the pre-consolidated slurry into a rubber mold prior to isopressing.

1 Introduction

PDMS stamps and molds, introduced by the Whitesides group¹, have been widely used in micropatterning of ceramics powders^{2, 3} and precursors to ceramics⁴⁻⁶ and several techniques have been reported. Gauckler and coworkers^{2, 3} have produced zirconia, cerium gadolinium oxide, tin oxide and alumina surface patterns by casting a high solid loading aqueous suspensions into PDMS molds. PZT sensor arrays were made by Rosquist and Johansson⁷ by a similar method. However, because the slurries used to fill the channels contained relatively low volume fractions of powder (0.40 to 0.50 volume fraction), long drying periods were required to avoid cracking because the shrinkage of the powder within patterned channels is constrained during consolidation via drying.

Previously, we have shown that small surface features, for example, the features on a one-dollar coin and 20 μm wide and 1 μm deep channels, could be rapidly produced on the surface of alumina powder compacts using Colloidal Isopressing.⁸ This ceramic forming method was first developed by Yu and Lange⁹, in which a pre-consolidated slurry is injected into an elastomeric mold and isopressed to rapidly convert the slurry into an elastic body that can be removed from the mold without shape distortion. The pre-consolidated slurry is initially formulated at a low volume fraction with chemical additives needed to produce a short-range repulsive potential between the particles. The short-range repulsive potential helps prevent the particles from forming a touching particle network when consolidated at low pressures. After the pre-consolidate body is fluidized via vibration, it is injected into a rubber mold, and isopressed at a high pressure, which forces the particles into contact and produces the elastic body shaped as the rubber mold. To allow the particle network to support the applied pressure, a small amount of liquid is removed from the pre-consolidated slurry as it further consolidates to form the elastic body during isopressing. Besides its ability for rapid forming, bodies produced by Colloidal Isopressing do not shrink during drying, which allows direct heating to the densification temperature.

When smaller surface features such as micron size channels were attempted, a problem was encountered where thin, deep features would fracture during either pressure release (differential strain recovery) or demolding. This problem is illustrated in Fig. 1, which shows a micro-turbine produced with alumina powder using a PDMS mold obtained from a micromachined silicon master through the Spearing Group at MIT. As shown, all of the features of the mold were reproduced (even defects), but the edges of the very thin static turbine vanes (see insert) were broken. The height of the vanes, fixed to the surface, were approximately 200 μm . The width of the larger vanes ranged from 800 μm to 60 μm , and the average width of the smaller vanes was about 100 μm . One method of solving this problem was to strengthen the powder compact. Since differential strain recovery (different elastic expansion of the PDMS material relative to the consolidated

powder compact) is one cause of stress, it was essential to increase the strength of the saturated, powder compact.

Literature suggests that significant effort has been extended to increase the strength of dry powder compacts, for example by using different binders^{10, 11}. Since the object of the current need is to increase the strength of the saturated powder body without reducing the viscosity of the pre-consolidated slurry, a different approach was sought. Morissette and Lewis¹² developed a gelcasting methodology based on aqueous alumina-poly(vinyl alcohol) (PVA) suspension, which was cross-linked by an organotinane coupling agent. They found that the gelation was concentration dependent, i.e., at a given PVA content, there was a critical titanium concentration below which the gelation would not take place; also, this critical titanium concentration decreased as the volume fraction of alumina increased. In the current work, it is demonstrated that this concentration-induced gelation can be applied to the Colloidal Isopressing method such that the gel transition will not take place until the isopressing step. As reported below, the viscosity of the pre-consolidated slurry is not significantly affected, yet the strength of the isopressed body was significantly improved to enable patterning of alumina surfaces patterns with a feature size as small as 5 μm and with an aspect ratio of 2.

2 Experimental

2.1 Colloidal Isopressing and mold fabrication

Aqueous α -alumina (0.20 volume fraction, 0.2 μm diameter, AKP 50, Sumitomo Chemical Co., Ltd., Japan) slurries were formulated as repulsive particle networks at pH 4, rolled for 16 h before adding 0.25M ammonia chloride (Fisher Chemicals, Fair Lawn, NJ, analytical grade) to create a weakly attractive network. The pH was adjusted (± 0.1 pH units) with analytic grades of either HCl or NH_4OH . For the gelation system, PVA Airvol 205 (Air Products and Chemicals, Inc.) was added to the slurry at 1 weight percent (relative to the alumina) and stirred for 30 min. Different slurries were formulated containing different volumes of Tyzor® TE (Dupont Chemicals, Deepwater, NJ), the coupling agent, which was added by pipet into the slurry and stirred for another 30 min. After this period, the pH was readjusted to 4 before pre-consolidation step.

As described elsewhere¹³, the slurry was pre-consolidated by pressure filtration at 5 MPa, which resulted in a cylindrical body 45 mm in diameter that was fluidized within a sealed, plastic bag (to prevent drying) by placing it on a tube vibrator. The relative density of the pre-consolidated slurry was determined to be 0.570 ± 0.0014 by the weight loss method (weight before and after drying, and heating to 500 °C to remove the volatile salt).

PDMS (Sylgard® 184 Silicone, Dow Corning Corporation, Midland, MI) molds were fabricated by casting a mixture of a silicone base and a curing agent at weight ratio 10:1 upon masters of desired surface features. The masters were made on silicon wafers patterned by either photolithography, micromachining or other methods. The liquid elastomer was degassed with vacuum and cured either at room temperature or upon heating to 70°C. Upon curing, the PDMS mold could be easily peeled from the master.

The pre-consolidated slurry was poured into the PDMS mold. The slurry was vibrated for 1 minute to allow bubbles trapped during pouring to rise to the top (despite its high relative density, the viscosity of the pre-consolidated slurry exhibits shear rate thinning, and greatly decreases its viscosity during vibration). To adsorb a small amount of water during isopressing, a dry pad of AKP50 (previously dry pressed at 10 MPa) with the same diameter as the mold cavity was placed on the top of the pre-consolidate slurry. After sealing, the filled mold was subjected to iso-static pressure of 200 MPa, (Isostatic Press, Autoclave Engineers Inc., Erie, PA) for a period of 2 min, a pressure much greater than the plastic-to-elastic transition pressure needed to convert the pre-consolidated slurry to an elastic body¹⁴. After the pressure was released and the mold removed from the iso-press, the body was elastic and could be removed from the mold.

2.2 Measurement of TE and PVA Concentrations

An aqueous solution containing the same amount of DI-water and the TE coupling agent as those in the initial 20 vol% alumina slurry were formulated to mimic the concentration of the TE in the initial slurry. As the 20 vol% alumina slurry was pre-consolidated, the filtrate liquid was collected to enable the measurement, by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer, of the TE coupling agent lost during

pressure filtration, and thus, that retained within the powder compact. Likewise, aqueous PVA standards were formulated.

The concentrations of PVA in the standard and in the filtrate collected during pressure filtration were determined by UV/VIS Spectrometer (Perklin Elmer). Because the reaction between PVA and iodine in dilute aqueous solution produces a blue color, the concentration of PVA is linearly related to the extinctions at the absorption maximum.¹⁵

2.3 Strength Measurement

Alumina bars were made by colloidal isopressing with dimensions of 0.3cm x 0.4 cm x 3.5cm. Tests were performed in 4-point bending (inner and outer spans, in cm) using the Instron 8562 and 1123 coupled with a 44.5 N (10 lb) load cell (Eaton Corp., Model 3108-10) immediately after the bars were removed from the mold after isopressing. The specimens were loaded to failure with a crosshead speed of 0.5mm/min.

3 Result and Discussion

The ICP measurement, as referenced to the standard, showed that the concentration of the formulated slurry contained 150 ppm of Ti. However, measurements of the filtrate produced after pressure filtration showed the concentration of Ti was 0.25 ppm, suggesting that nearly all of the TE coupling agent was retained in the consolidated powder compact. Since the volume fraction of the alumina increased from 0.20 within the slurry to 0.57 after pre-consolidation, and then to 0.64 after isopressing, the concentration of the TE coupling agent at each stage could be calculated based on the initial amount added and the volume of water lost. Fig 2 shows the change of the concentration of TE after pre-consolidation and after isopressing in a 20ml 0.20 volume fraction slurry with different volumes of TE added at the beginning. For example, if a slurry is formulated with TE100 ul TE coupling agent (initial [Ti] is 97ppm), then after pre-consolidation, the [Ti] is increased to 276 ppm and after isopressing, to 310 ppm, namely a 3 fold increase from that in the initial slurry.

The UV measurement showed that the concentration of the PVA in the filtrate was 88% of that used to formulate the initial slurry. By calculation, the concentration of PVA only slightly increased within the powder compact after pre-consolidation; the increase was so small that to the first approximation, the concentration of PVA did not change.

Since the volume fraction of the alumina increased, the condition of the PVA-TE-alumina system in our Colloidal Isopressing method was similar to that needed to form a gel through concentration change as described by the Lewis group¹².

As shown in Fig 3 significant strengthening was achieved. As the TE concentration increased, so did the strength of the saturated, consolidated body. The bars fabricated with slurries formulated at pH 4 exhibited even greater strengths than those formulated at pH 5 or 6.

As a comparison, Fig 4 shows the results of our previous, unreported work concerning the strength of saturated powder compact, produced by Colloidal Isopressing, where only PVA was added to the slurries formulated at pH 4 in an identical manor reported here. The figure shows that the strength decreased for the saturated powder bodies with increasing PVA. Even though the strength after drying increased with additions of PVA, the dry strength was lower relative to the saturated strength. Previous studies¹⁶ have attributed the greater strength of saturated bodies, relative to dry bodies, to the plastic deformation that occurs at the crack front in saturated bodies. Namely, when saturated bodies are subjected to large strains, the touching particle network can be pulled apart to re-establish the pair potential prior to consolidation. This phenomenon can produce a large crack growth resistance. Because of the larger crack growth resistance, the saturated body has a higher strength relative to the dry body. In addition, since the PVA is more likely to form hydrogen bonds with water instead of with the alumina particles, there is no strong network between the alumina particles in the saturated bodies.

The PVA-TE methodology is effective for increasing the wet green strength of the isopressed body, while at the same time, not increasing the viscosity of the pre-consolidated body. As the wet green strength increased, feature sizes as small as 5 μm could be duplicated very successfully as shown in Fig 5, which shows channels with an aspect ratio of 2:1. The material between the channels is similar to the the tip of the damaged micro-turbine vane shown in Fig 1, but with a feature size one order of magnitude smaller. Features this small and 0.4 cm long could be fabricated without damage during either pressure release after isopressing or demolding.

4 Conclusion

A new microfabrication method of ceramics using Colloidal Isopressing has been improved by formulated a slurry containing additives that form a gel once their concentration is increased during the final consolidation step. The Colloidal Isopressing method is a rapid forming method and since there is no shrinkage during drying the consolidated body can be dried very fast. The major problem of this process is cracking during either pressure release or demolding. The concentration induced gelation of the PVA-TE system significantly increases the wet green strength of the ceramic body while maintaining a low viscosity of the pre-consolidated slurry. Feature sizes of 5 μm and aspect ratio of 2:1 on alumina powder surface were obtained using slurries formulated with a weakly attractive particle network and the PVA-TE gelling system.

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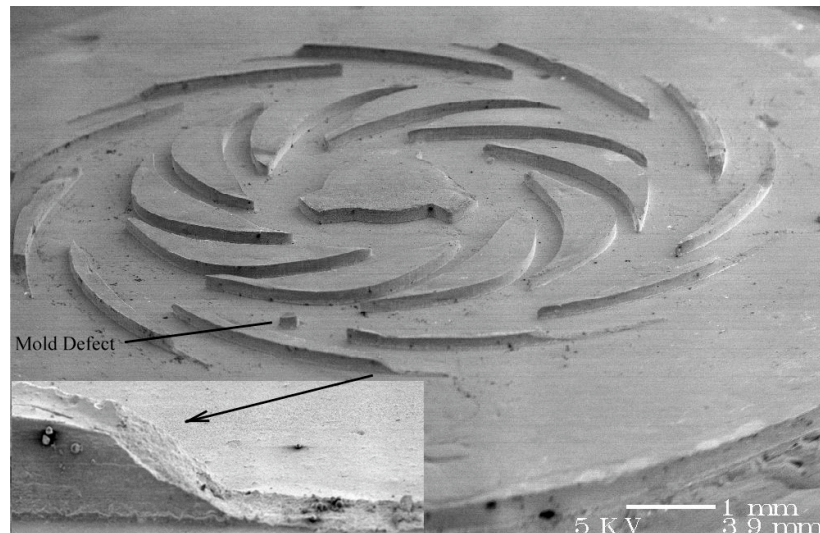


Figure 1 SEM of the isopressed, dried and sintered micro-turbine. Insert shows that the thin tips of the turbine vanes are fractured during de-molding.

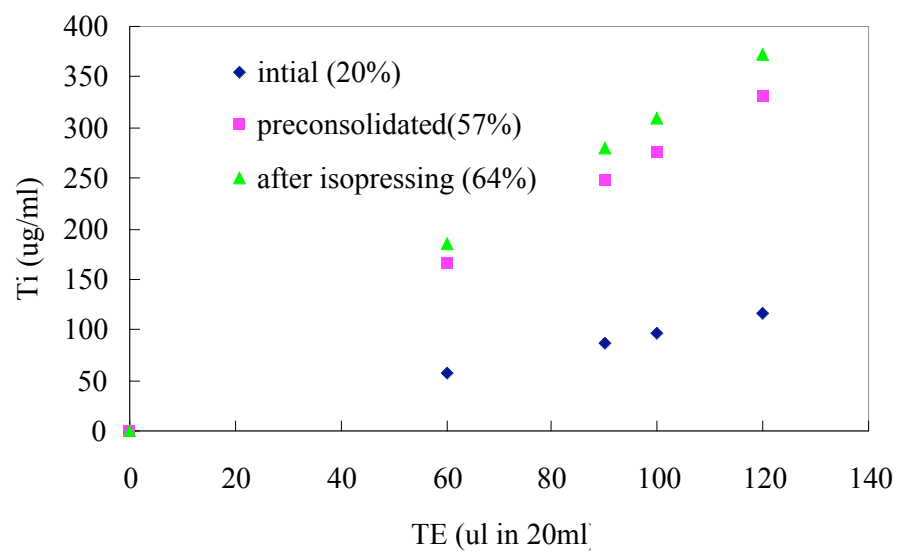


Figure 2 Concentration calculation of Ti in pre-consolidated body and isopressed body based on that in the initial slurry

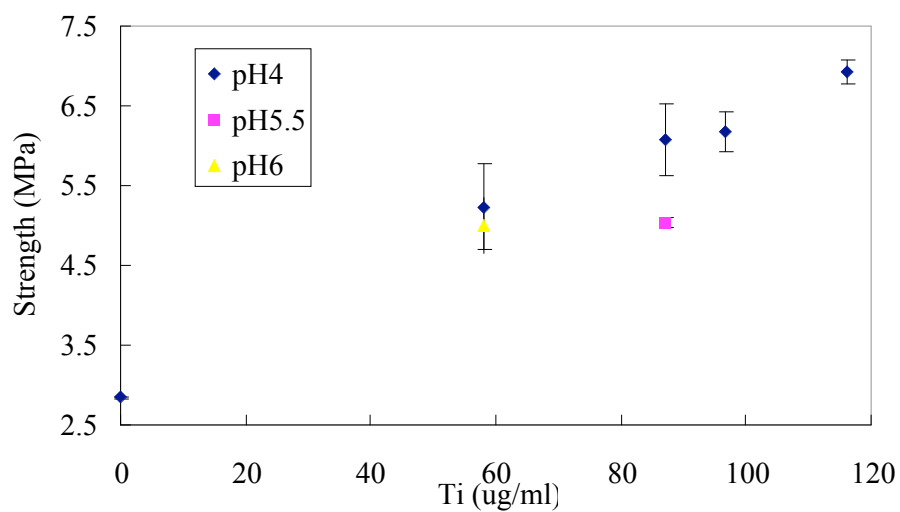


Figure 3 Flexural strengths of saturated alumina bodies with different concentrations of Ti molecule; PVA was fixed at 1wt% of alumina powder in the slurry

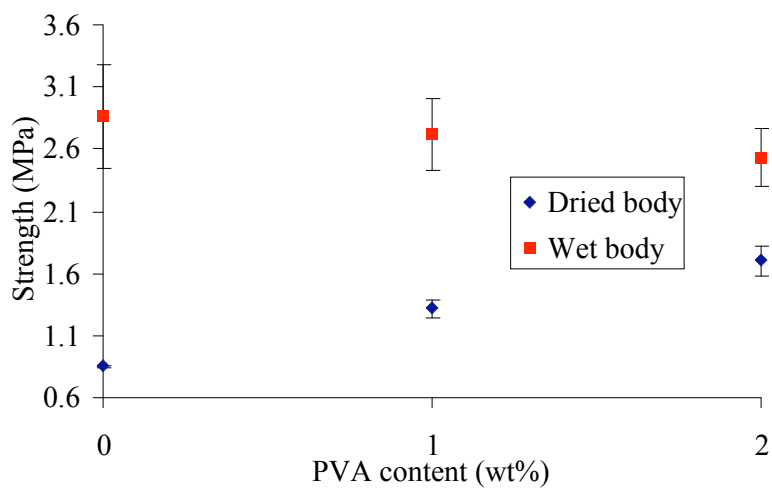


Figure 4 Green strengths of wet and dry bodies with different PVA concentration at pH4

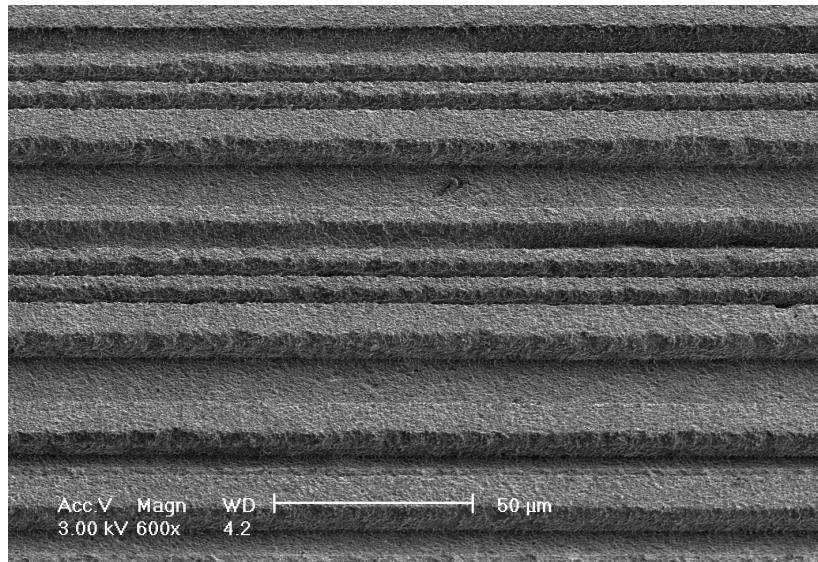


Figure 5 (a) SEM of surface features as small as 5 μm; height of features is 10 μm.

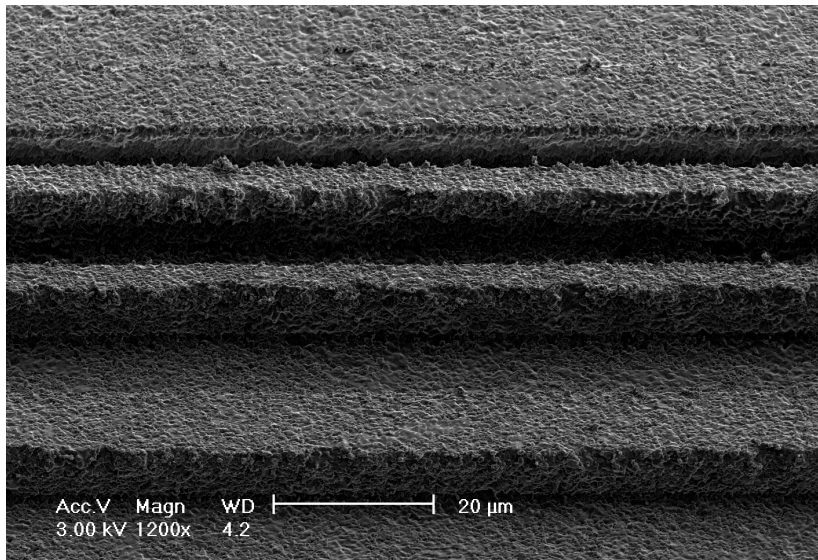


Figure 5 (b) Enlarged features.

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